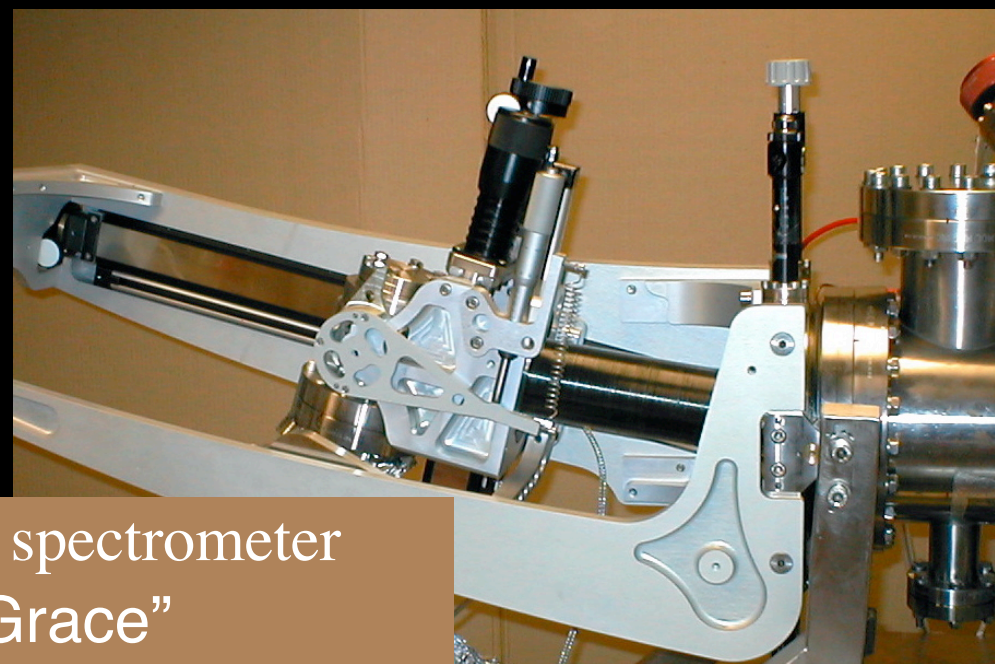


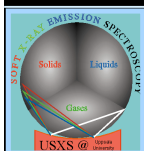
Entering a new phase: Studying liquids with RIXS at the ALS

by Laurent Duda,
USX group, Uppsala University

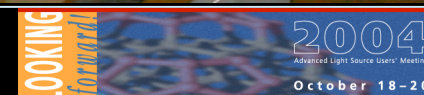
- Our *liquid flow cell* project
- Examples of recent "*liquid button cell*" (and other) experiments
- Our *QCM cell* project: *atmospheric corrosion* layer by layer
- *Summary and conclusions*



Uppsala spectrometer
"Grace"

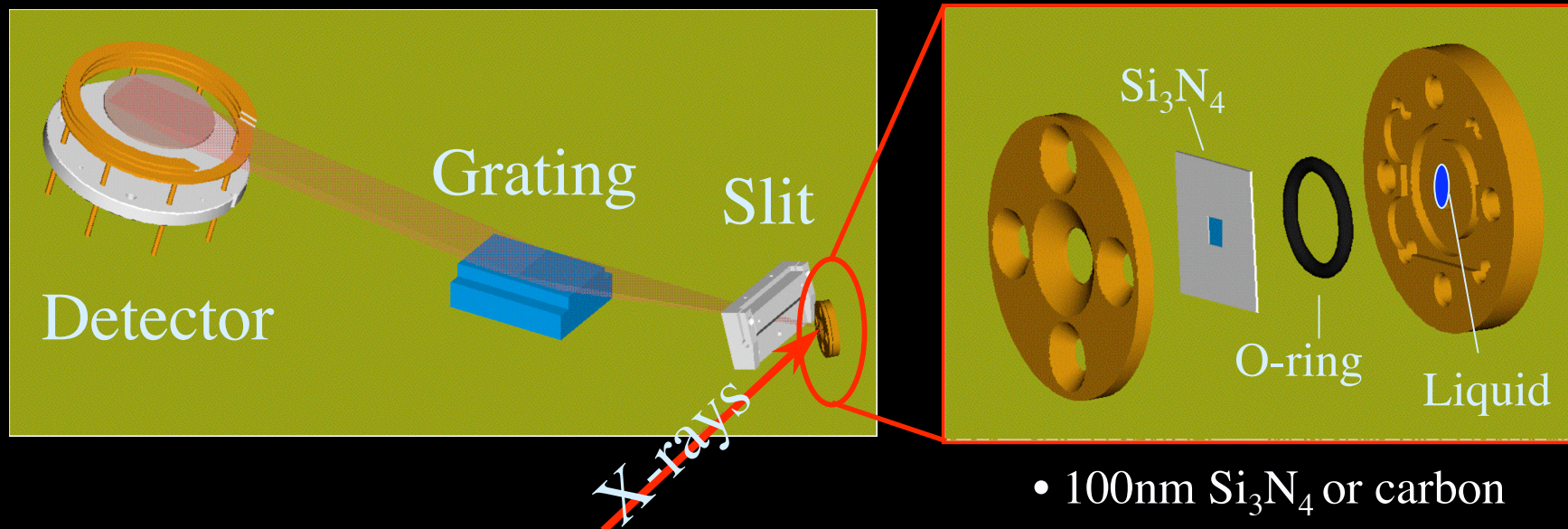


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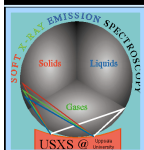


Experiments with X-ray-window sealed liquid "button" cells

Our "button cell"



- 100nm Si₃N₄ or carbon
- ~4 μ l sample,
- 30% transmission @ O1s



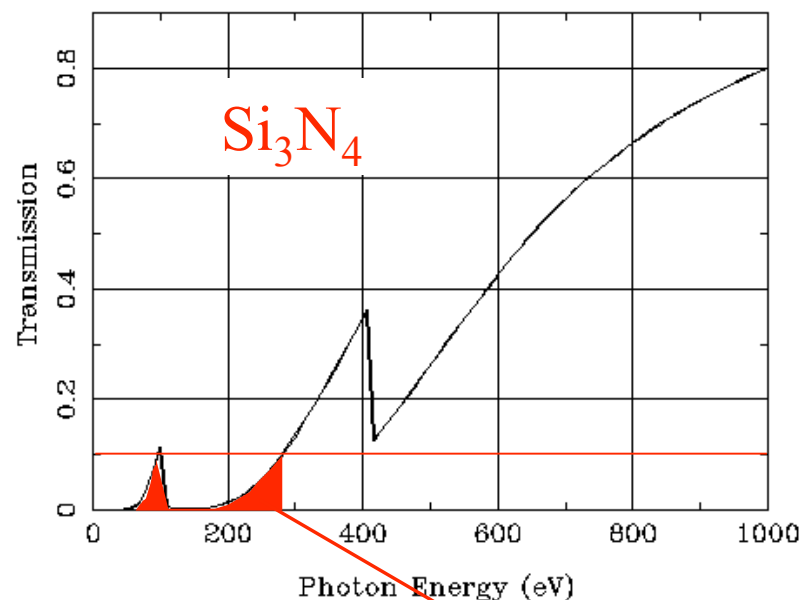
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Experiments with X-ray-window sealed liquid "button" cells

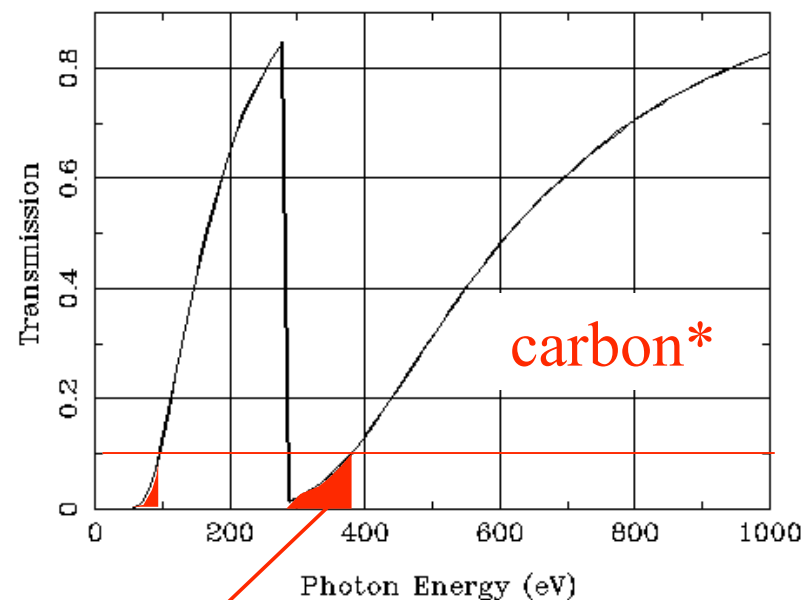
Transmission of x-rays by

Si₃N₄ Density=3.44 Thickness=0.283 microns



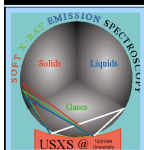
Transmission of x-rays by carbon

C Density=3. Thickness=0.283 microns



"Dark" regions

*manufactured by Joakim Andersson, Uppsala



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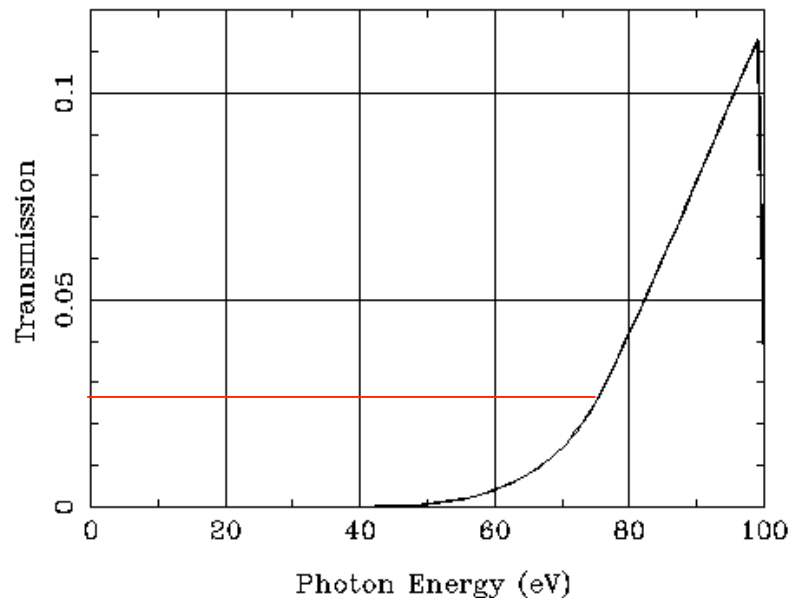
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Experiments with X-ray-window sealed liquid "button" cells

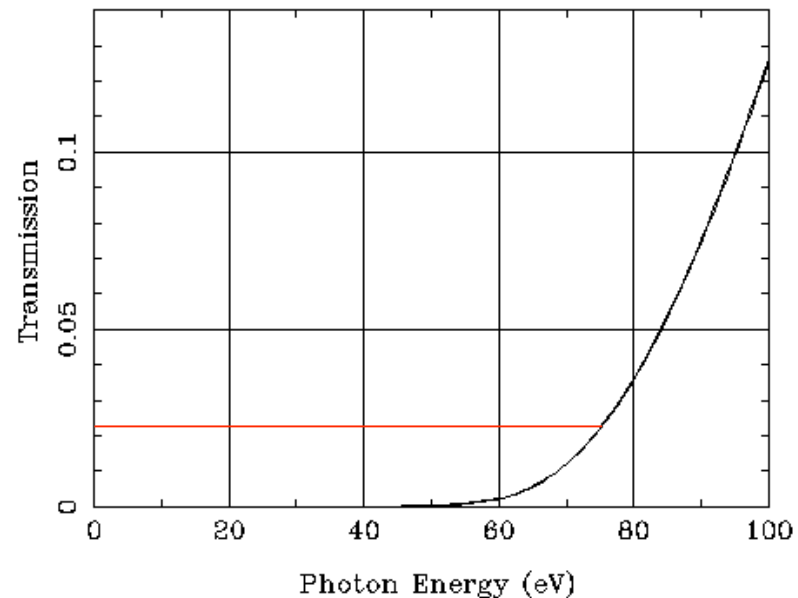
Transmission of x-rays by Si_3N_4

Si_3N_4 Density=3.44 Thickness=0.283 microns



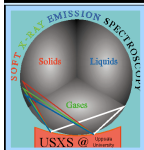
Transmission of x-rays by carbon

C Density=3. Thickness=0.283 microns



Problematic low energy region: 2-3% transmission for Cu 3p-edge

Need other material: boron?

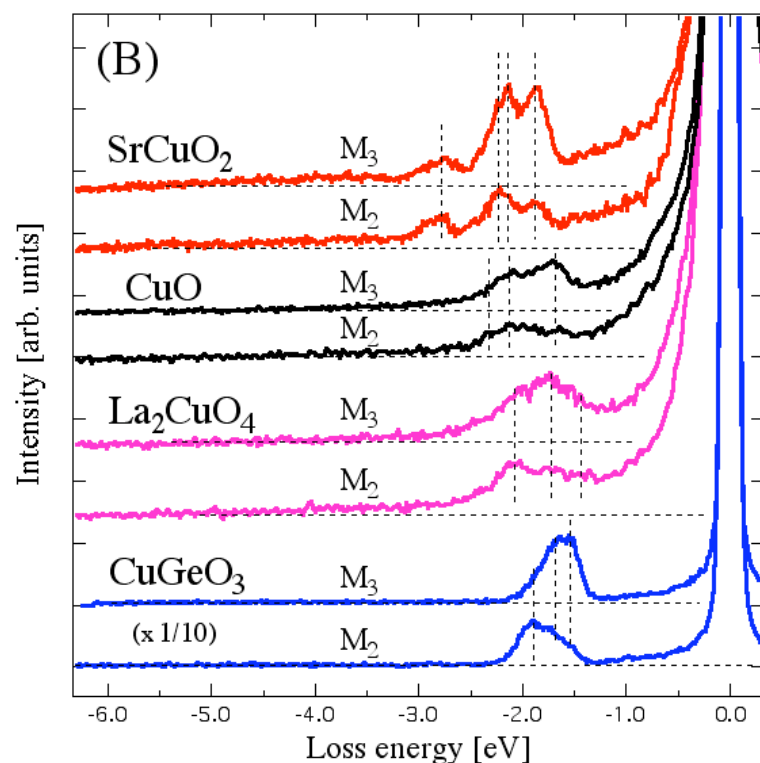
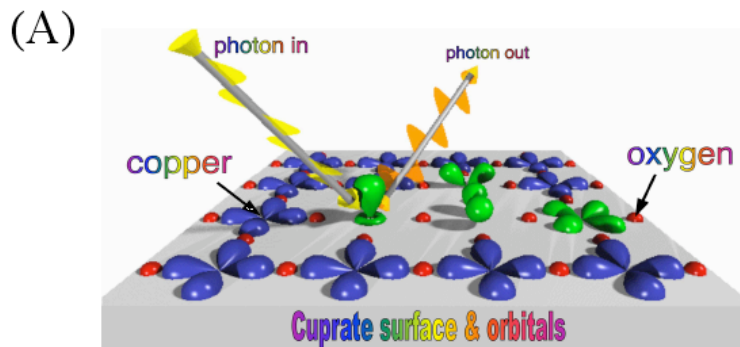


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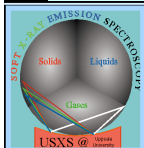
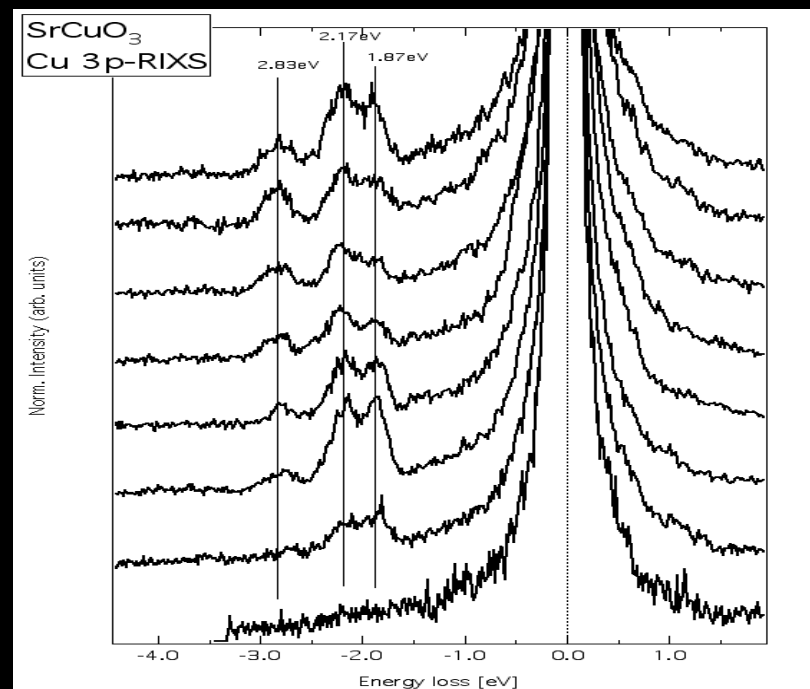
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Low energy ultra-high resolution RIXS at Cu M-edges



L.-C. Duda et al. To be published

Energy dependent RIXS



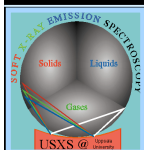
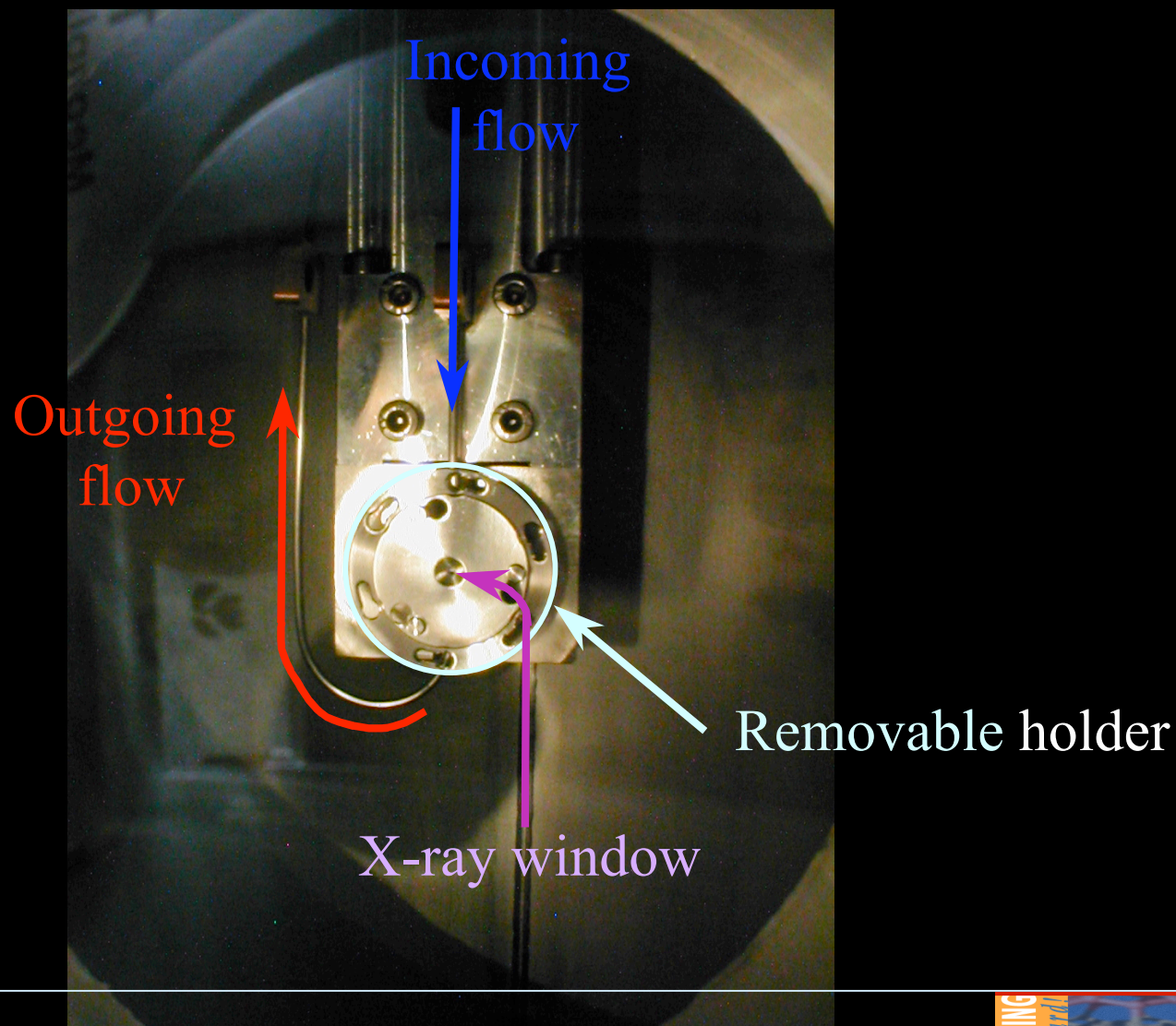
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Flow-cell for studies of fluid samples

View into vacuum chamber:



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Flow-cell for studies of fluid samples

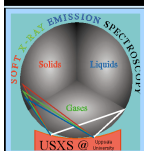
Key features:

Controlled *flow rate* past window

Window *removable in situ* for making films and measuring on backside

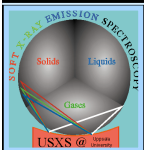
Temperature control of liquid

Application of an *electrical potential* to window



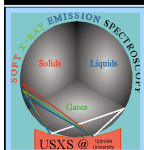
Flow-cell for studies of fluid samples

- Prototyp:
built and in testing stage
- Control/feedback system:
Labview-based
- Window breakage safety valve:
Reseals in tens of microseconds



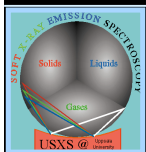
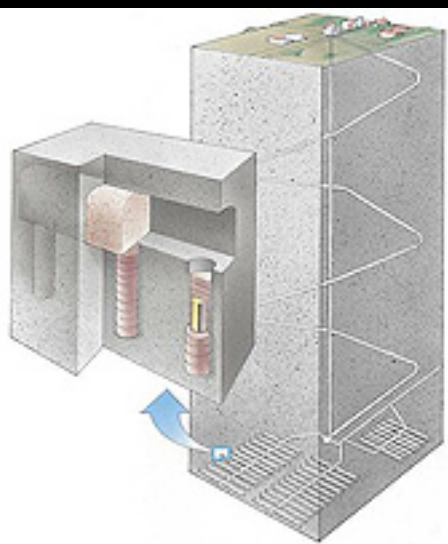
Examples for possible types of experiment

- Quick *in situ* change of liquid type or concentration
- Electrochemical cells and batteries
- Corrosion processes of wet surfaces
- Hydrogen loading of thin films
- Mixing of multiple components and monitoring chemical reactions



Project: Nuclear waste storage canisters

- SKB (Adj. Prof. L. Werme)/Uppsala
- RIXS on actinide oxides
- sulphide and chloride reactions with copper



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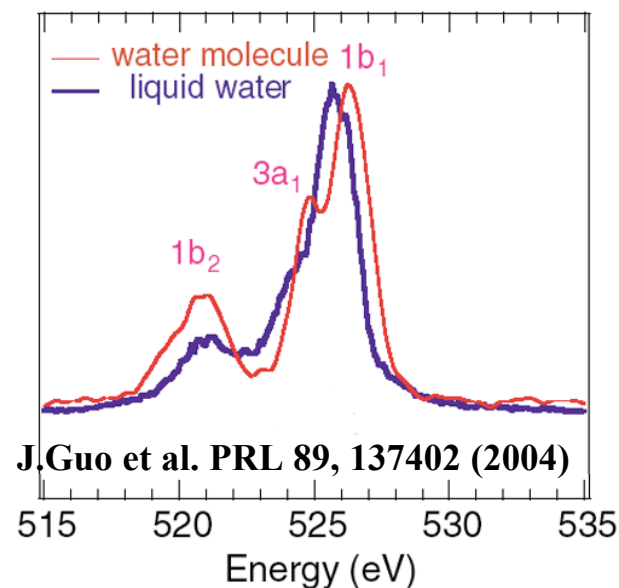
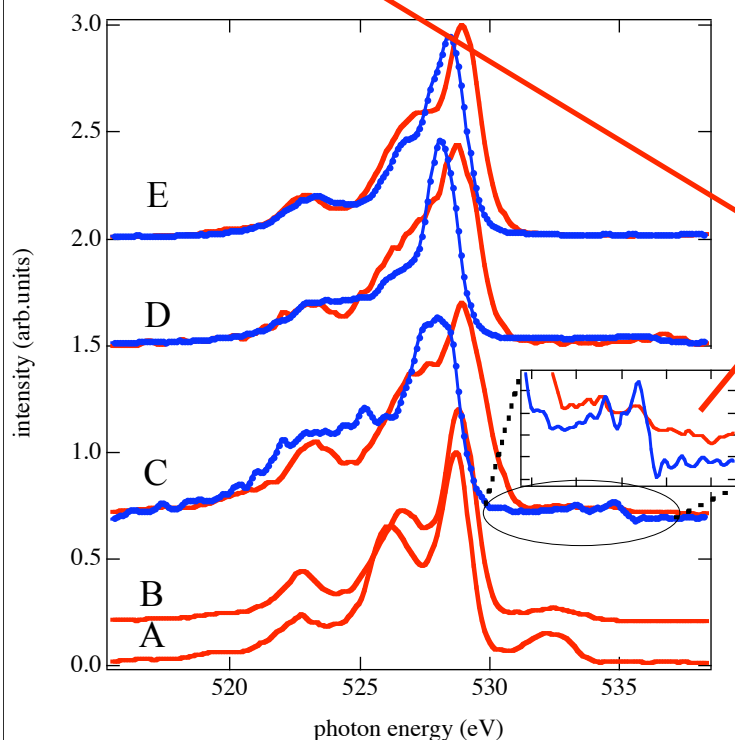
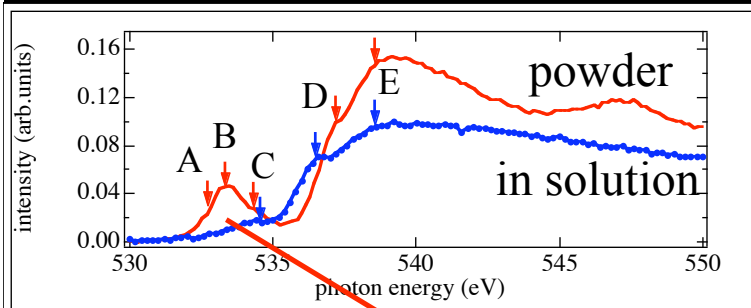


Experiences with our *button cell*: results and surprises

Concentrated solution of CuSO_4

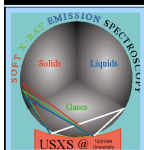
O1s absorption

Interaction
between water
and Cu 3d-
orbitals



J. Guo et al. PRL 89, 137402 (2004)

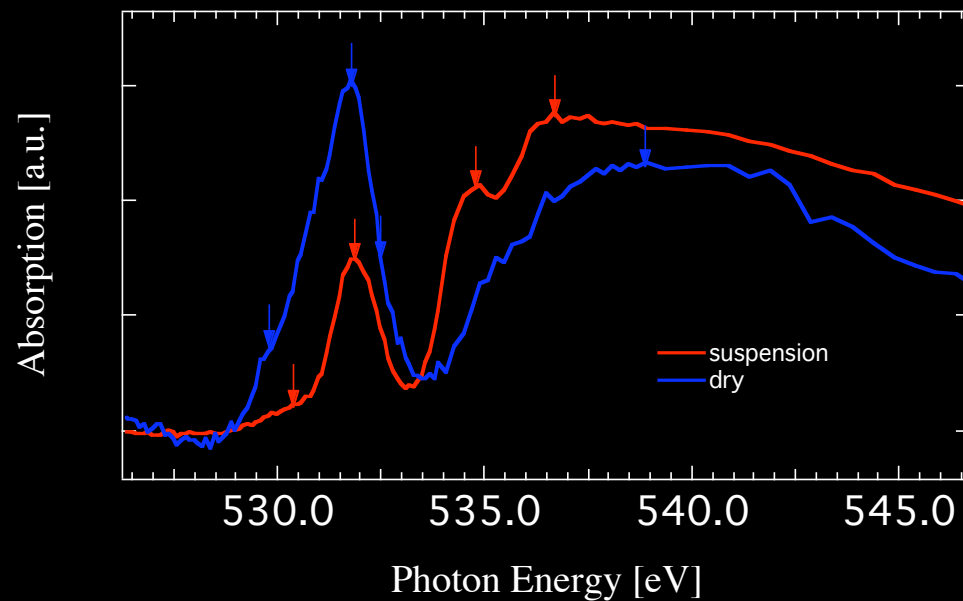
O1s resonant emission



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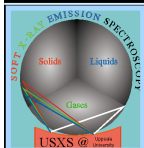
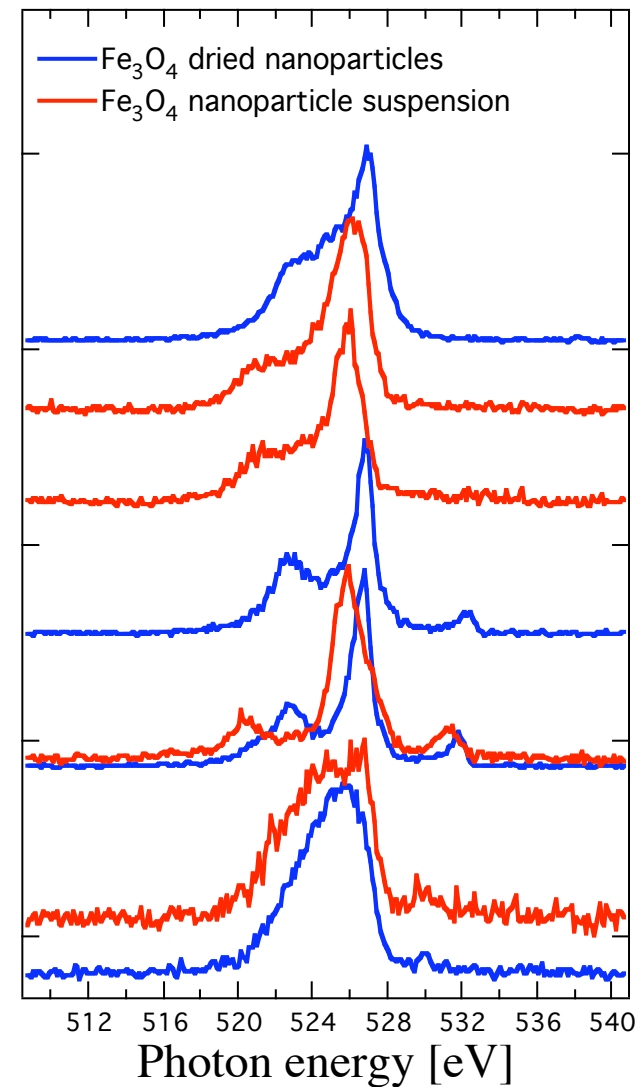


Fe_3O_4 nanoparticles in a water suspension*



* Fe_3O_4 nanoparticles grown by Dr. Lionel Vayssieres

$\text{O}1\text{s}$ -RIXS



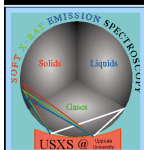
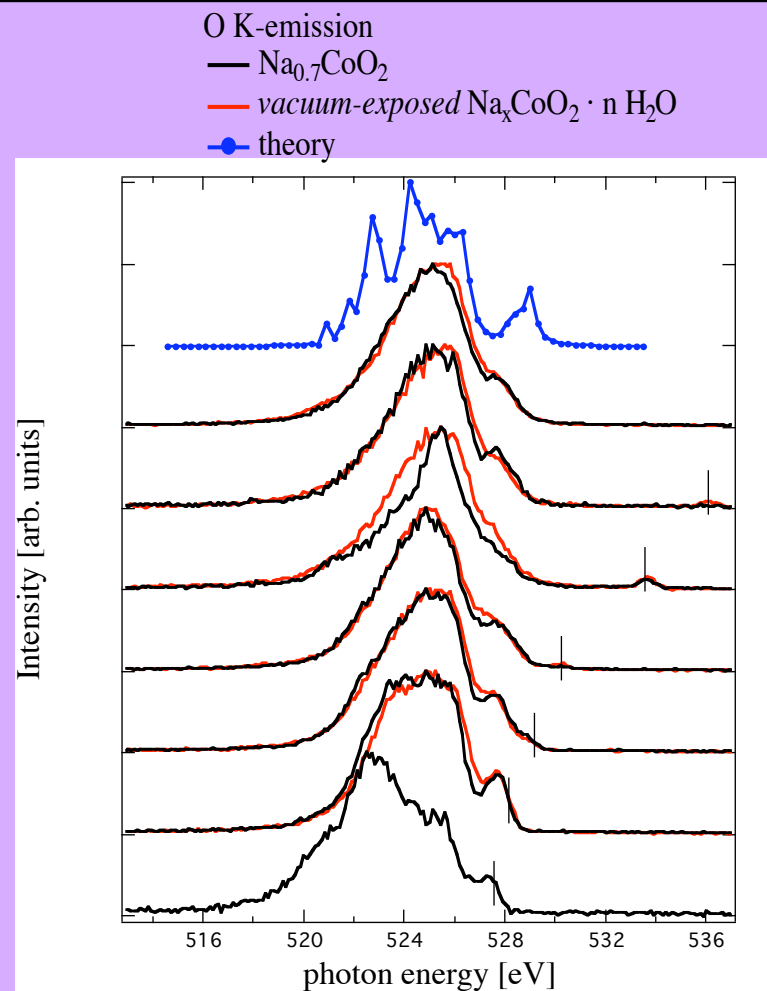
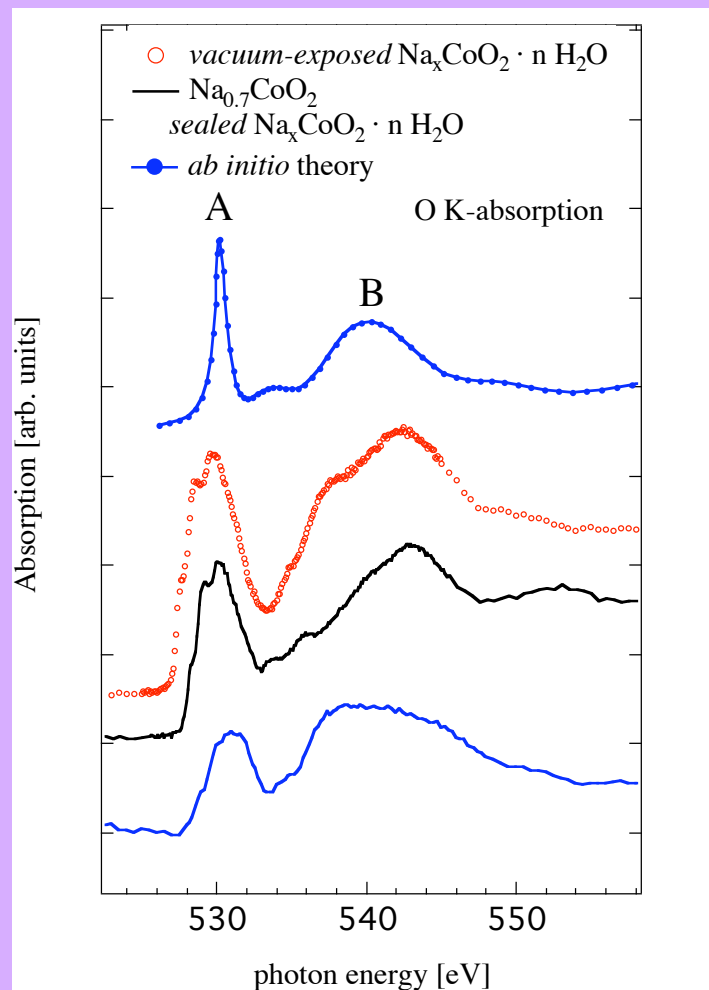
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Hydrated materials lose water in vacuum

Sodium cobaltates

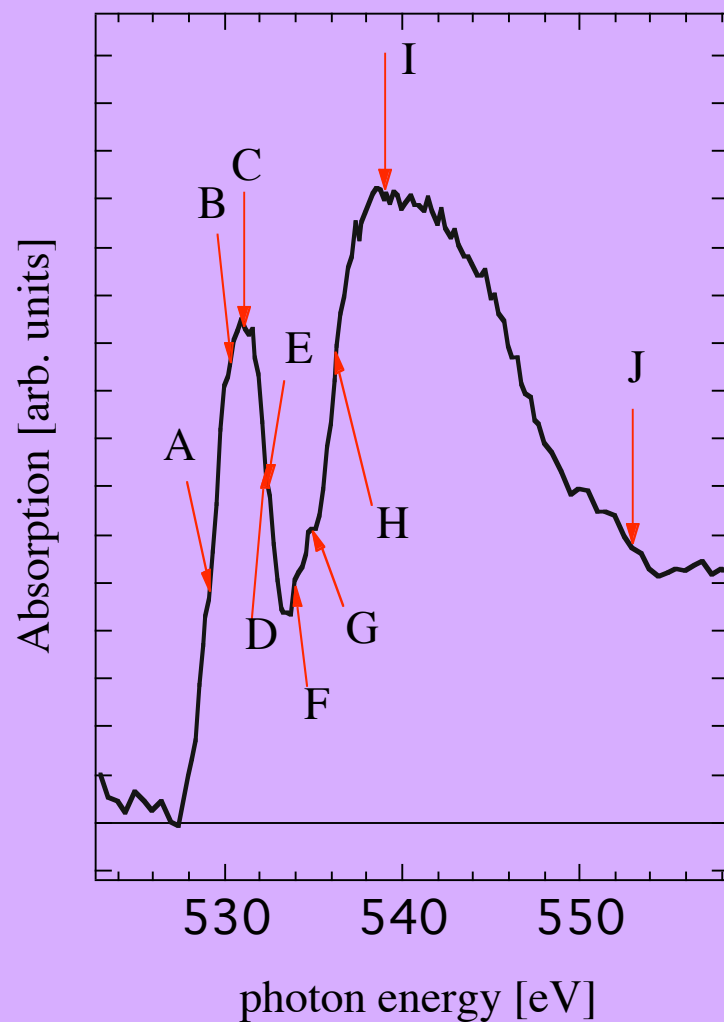


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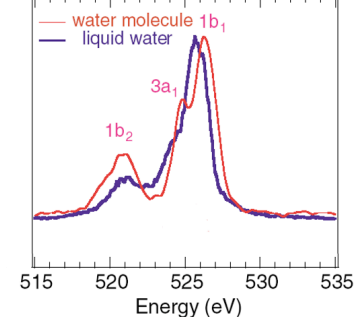
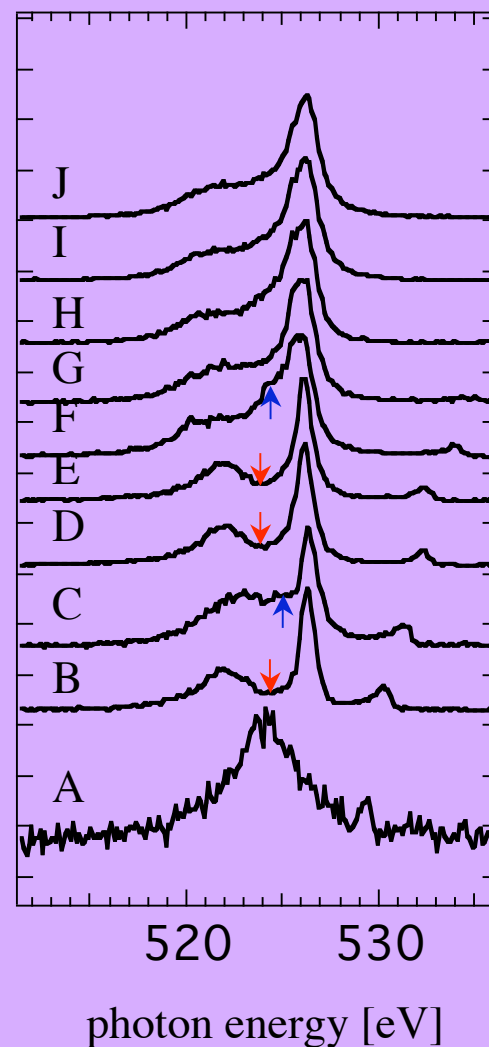
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Hydrated materials lose water in vacuum

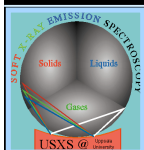


Emission Intensity [arb. units]



J.Guo et al.

PRL 89, 137402
(2004)



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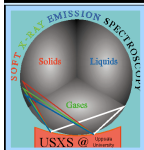
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Trapped *bubbles* and *pressure build-up* in button cell

An attempted study of H_2O_2 ...

...turns into an actual measurement of O_2 ...

...and calls for the use of our new *flow cell*.



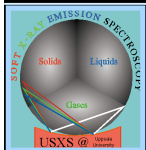
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QCM gas cell for studies of atmospheric corrosion

- Uppsala/Stockholm collaboration (VR funded)
- metal films grown in situ on QCM
- study of surface degradation from a flow of corrosive air
- simultaneous *in situ* monitoring of mass change and SXES



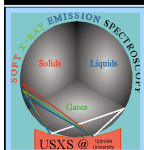
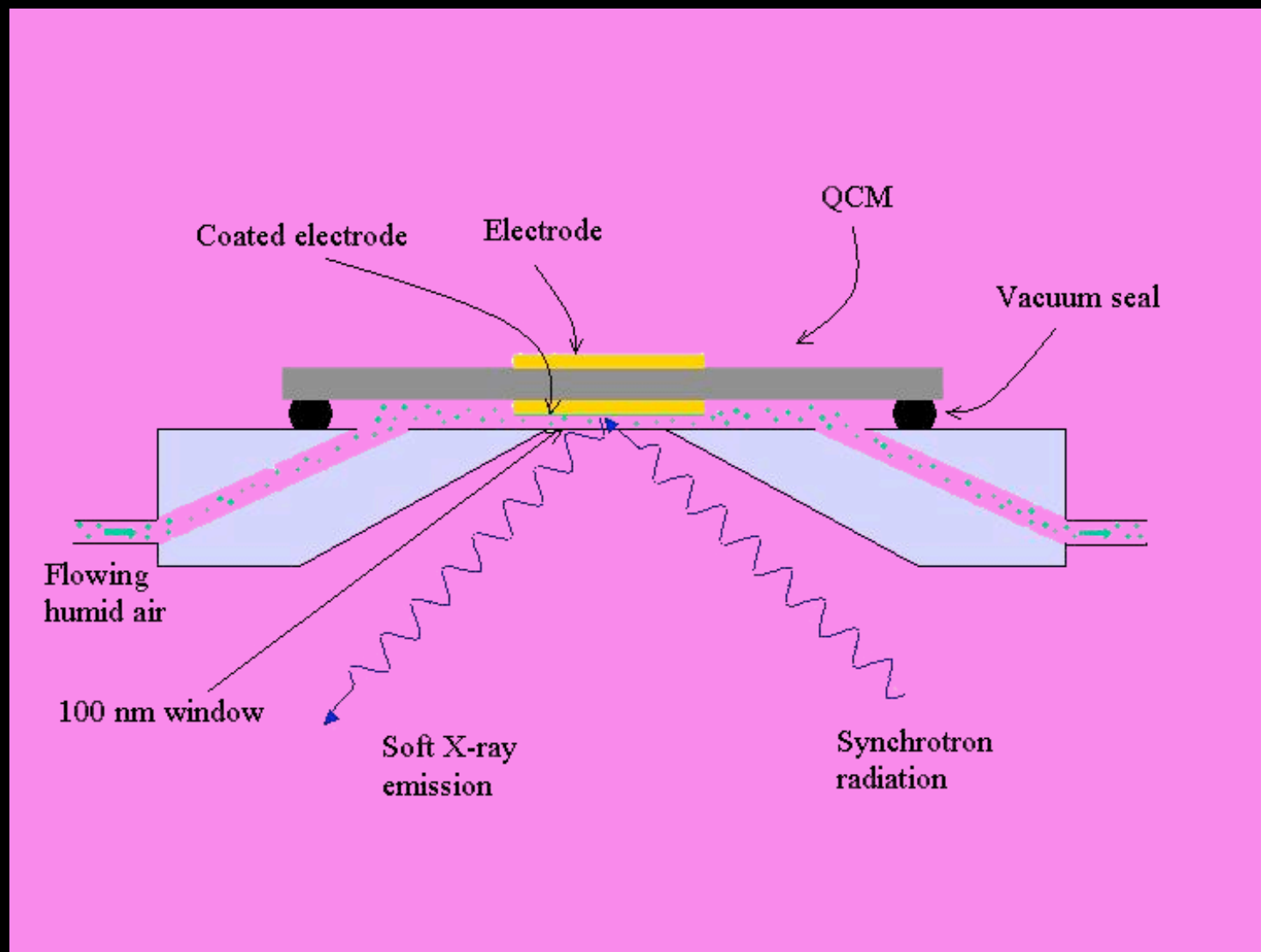
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Schematic view of the *QCM Gas cell*

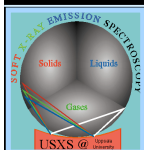
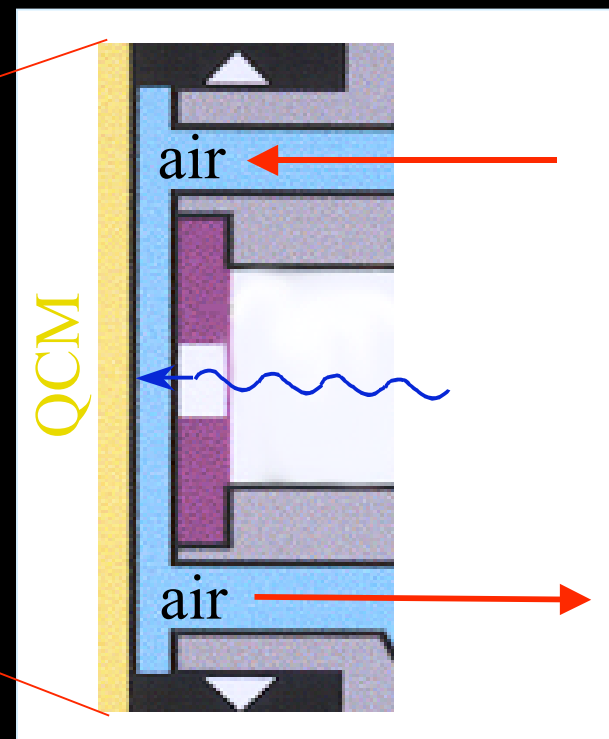
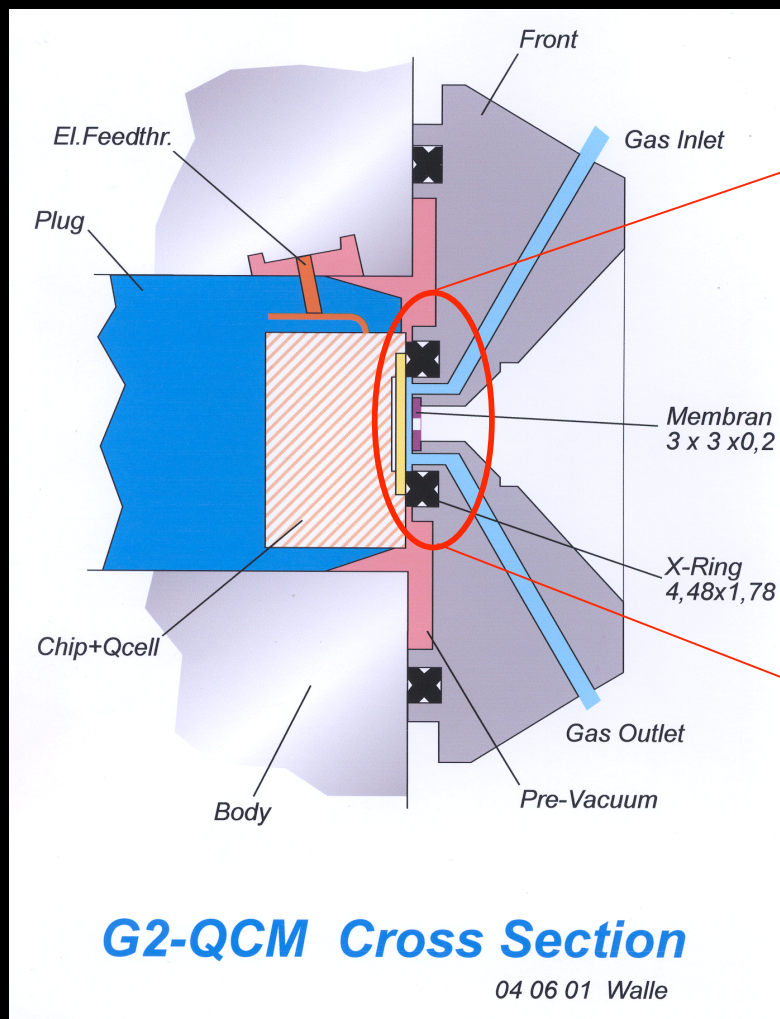


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Schematic view of the *QCM Gas cell*



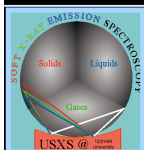
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Status quo

- Prototype both *vacuum-tested* and *QCM*-tested
- *SR-version* designed and parts are in machine shop (*due Oct.*)
- First *synchrotron studies* planned in late Fall 2004



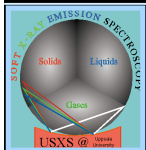
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Conclusions

- *Water-ion interaction* can be substantial in solutions
- *Window-technique* also important for *hydrated* solid materials
- *Button cell*-experiments simple but limited (&surprises)
- Two versatile *flow cells* for *wet/gaseous* environments



Acknowledgements

Prof. J. Nordgren, head of USX group

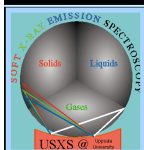
Collaborations (exp.): Prof. C. Leygraf, Dr. T. Aastrup, Prof. U. Karlsson, Prof. L. Werme

Collaborations (theor.): Dr. R. Ahuja, Dr. M. Mattesini, P. Kuiper, C. de Graaf

PhD students: A. Augustsson (now PhD), T. Schmitt (now PhD),
J. Forsberg, J. Söderström, K. Kvashnina

ALS beamline assistance/collaboration: Dr. J. Guo

Samples and technical development: Dr. L. Vayssieres, Dr. J. Andersson



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